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The Determination of
Sulphur in Steel

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THE DETERMINATION OF SULPHUR IN STEEL

BY

ROSS McGEHEE STIFF

THESIS

For the Degree of Bachelor of Science

in Chemistry

College of Science

University of Illinois

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June 1, 1908.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

R. M. STIFF

ENTITLED THE DETERMINATION OF SULPHUR IN STEEL

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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TABLE OF CONTENTS.

	Page
Introduction-----	1
Oxidation Methods-----	5
Gravimetric Evolution Methods-----	16
Volumetric Evolution Methods-----	20
Colorimetric Methods-----	23
Summary-----	25
Object-----	25
Experimental-----	28
Conclusion-----	35
References-----	36

THE DETERMINATION OF SULPHUR IN STEEL.

Introduction.

The processes for the determination of sulphur in iron and steel may be divided into two general classes: (1), The oxidation methods; (2), The evolution methods.

The oxidation methods are based on the principle that when the iron is treated with an oxidizing agent, the sulphur is changed to sulphuric acid, which may be precipitated with barium chloride. The methods using this principle are all gravimetric.

The evolution methods depend on the fact that when iron or steel is treated with hydrochloric or sulphuric acid, the sulphur is evolved as hydrogen sulphide. The sulphur evolved in this form may be determined volumetrically as hydrogen sulphide, or changed to a metallic sulphide and weighed as such, or passed through a solution of a metal and the color compared with standards.

In order to oxidize the sulphur to sulphuric acid in the presence of iron, the borings are fused with a basic mixture or treated with bromine, bromine and acids, hydrochloric acid and an alkaline chlorate, nitric acid, or a mixture of nitric and hydrochloric acids added singly or as aqua regia.

The gravimetric methods may be enumerated as follows:

1. The standard method of aqua regia decomposition.

2. Decomposition of the borings with ferric or copper ammonium chloride solution, and oxidation of the carbonaceous residue which contains all the sulphur by such reagents as are used to attack steel directly.

3. (a). Evolution as H_2S into solutions of KOH , $NaOH$, $KMnO_4$, $AgNO_3$, $HgCN$, H_2O_2 , bromine and HCl , and oxidation when necessary by the usual reagents.

- (b) Absorption of the H_2S by neutral or alkaline solutions of lead, oxidation to and weighing as $PbSO_4$.

- (c) Absorption of the H_2S in alkaline cadmium solutions, the sulphide being weighed; or the precipitated sulphide being added to copper sulphate and the resulting sulphide ignited to copper oxide.

- (d) Absorption of the H_2S in other metallic salts such as $AgNO_3$, the sulphide or some other form of the metal being weighed.

4. Fusion of the finely divided metal with sodium peroxide or with a mixture of magnesia and $NaOH$, dissolving out the alkaline sulphate and precipitating as usual. Or the addition of a little alkaline salt to the acid solution of the metal, ignition of the dried mass and dissolving the alkaline sulphate.

Both HCl and H_2SO_4 have been used to evolve the sulphur from steel. Dilute acids are sometimes used but

stronger acids are better, although they take more time. A mixture of the two acids dissolves the iron more readily than either acid used singly. It is admitted, now, that when the evolution process is used, sulphur is apt to be left in the residue. Phillips⁽¹⁾ has discovered that a portion is evolved as an organic sulphur compound, methyl sulphide, which is neither oxidized nor precipitated by ordinary reagents, and is only transformed into H_2S when passed through a red hot tube.

The more important reagents used for the absorption of H_2S and the modes of completing the estimations are;

1. Absorption by solutions of caustic alkali, cadmium, zinc, or potassium tri-iodide, and titration with iodine or thiosulphate.
2. Absorption in a neutral solution of metallic salt, and titration of the liberated acid.
3. Absorption in caustic alkali, addition to an acid solution of a reducible salt, (Fe_2O_3), and titration of the lower oxide formed.
4. Titration of the alkaline sulphide with a solution of an easily precipitated metal, lead nitrate.
5. Absorption in a solution of a metallic salt of Pb, Cu, As, and measuring the precipitated sulphide after whirling in a centrifugal machine; or assaying the undecomposed filtrate.
6. Passing the H_2S through a series of bulbs containing equal amounts of a standard lead acetate or $AgNO_3$

solution, as no two bulbs are discolored simultaneously, the result is obtained by counting the number of bulbs affected.

7. Comparing the color of a metallic plate or calico soaked with a metallic salt, or a solution of a metallic salt over, or through, or into which the H_2S has passed, with standards.

The evolution methods have a legitimate use in iron and steel works where time is a great factor, but not in commercial laboratories where the work must be accurate. An evolution method should never be used in case of dispute. It is a difficult matter to determine sulphur accurately. Even the most skilled chemists get varying results when using the same method. The following table ⁽²⁾ shows a series of experimental determinations of the sulphur in a sample of pig iron. The experiment was instituted by the Crane Iron Company. The analyses were made by various chemists of repute in the United States and Germany.

Method Used	Per cent Sulphur.
Nitro-hydrochloric acid -----	.005
Absorption and oxidation with bromine and weighing insoluble residue as $BaSO_4$ -----	.008
Absorption and titration with iodine- -----	.009
Absorption in alkaline solution of lead nitrate and weighing as $BaSO_4$ -----	.011
Aqua Regia method solution standing 24 hours-----	.012
Aqua Regia Method-----	.012
Absorption in $KMnO_4$ and weighing as $BaSO_4$ -----	.013

Absorption in CdCb_2 and titration with iodine-----	.013
KMnO_4 method, weighing as BaSO_4 -----	.013
Aqua Regia, neutralizing with NH_4OH standing 24 hours.	.013
Absorption in CdCl_2 and titration with iodine-----	.015
Absorption and titration with iodine-----	.015
Absorption and titration with iodine-----	.017
Absorption in KMnO_4 weighing as BaSO_4 -----	.017
Volumetric, no details given-----	.019
Absorption with $\text{Cd}(\text{CO}_4)_2$, titration with iodine-----	.020
Aqua Regia method-----	.021
Absorption in NaOH and titration with iodine-----	.022
Aqua Regia method-----	.024

The standard or aqua regia method is carried out as follows; ⁽³⁾ 5 grams of the borings are placed in an Erlenmeyer flask and 40 cc. of con. HNO_3 added, cover with a watch glass and heat on a hot plate, using an alcohol or a gasoline burner. The solution of the steel is hastened by the addition of a few cc. of HCl from time to time. When all the iron is in solution except, perhaps, a little graphite or silica, transfer to a casserole, add a little Na_2CO_3 , cover with a watch glass and evaporate to dryness, baking until all the HNO_3 is driven off. Cool, add 30 cc. of con. HCl , heat until the oxide of iron is dissolved and then evaporate to dryness to render the silica insoluble. Take up the residue with con. HCl just sufficient to dissolve the ferric oxide, dilute and filter. The sulphur is now in the filtrate in the form of sulphuric acid and is precip-

itated from a boiling solution with 10 per cent BaCl_2 . The precipitate is allowed to settle over night, then filtered, ignited, and weighed.

Ford and Wiley⁽⁴⁾ recommended the addition of NH_4Cl to the last solution just before filtering, since, if properly manipulated, it leaves the solution just acid enough and with enough NH_4Cl so that a complete precipitate of BaSO_4 entirely free from iron, is assured. They take up the baked mass from a 2 gram sample in 10 cc. of HCl , heat this to dissolve the iron salts and evaporate to 4 or 5 cc. They then add 5 g. of NH_4Cl ; this amount nearly or quite absorbs the HCl and, after the addition of water, filtering and washing, will leave about 75 cc. of solution in the filtrate with sufficient NH_4Cl and acid to insure a complete precipitation of the BaSO_4 .

Another method, not much used, is that of Lunge⁽⁴⁾ modified by Küster and Thiel and used by Hillebrand and others. The baked mass is dissolved in HCl , diluted with the same amount of water, filtered and washed, made slightly ammoniacal, 10 cc. of BaCl_2 added, then made slightly acid with HCl diluted to 300 cc., boiled down to 100 cc. and allowed to stand 12 hours. This method seems to give good results.

Meineke reduces the ferric chloride to the ferrous state with zinc before precipitation, to avoid contaminating the BaSO_4 with iron.

Archbutt⁽⁵⁾ says that the solution from which the

sulphur is precipitated in the aqua regia method should be concentrated. A concentrated solution of a steel containing 0.125 per cent of S. was divided into four portions. One solution was not diluted, while the others were diluted to 250 cc., 500 cc., and 750 cc. To each solution 5 cc. of a 10 per cent solution of BaCl_2 was added and the solutions stood about twelve hours before filtering.

Volume of Solution.	Percentage of Sulphur
63 cc.	0.125
250 cc	0.114
500 cc	0.091
750 cc	0.074

He then tried experiments to see whether free acid was detrimental. 5 grams of steel were treated in the usual manner except the HCl was evaporated off from the final solution. Duplicates were run in the same manner except, before adding BaCl_2 , 5 cc of HCl (1.1 sp.gr) were added to each concentrated solution.

No. of Sample	Neutral Solution 60 - 70 cc. Per cent of Sulphur	Acid Solution. 60 - 70 cc Per cent of Sulphur
1	0.146	0.142
2.	0.114	0.114
3.	0.082	0.087
4.	0.067	0.067
5.	0.059	0.056

Having shown that precipitation should be effected in a concentrated solution and that the presence of free HCl is beneficial, he then tried to determine the length of time necessary for complete precipitation. Sample No. 1 of the last series was used. Both solutions were treated exactly alike, the sulphur being precipitated from both solution. Only one stood 2 hours and the other 3 hours after precipitation.

Acid Solution
60 - 70 cc.
Per cent Sulphur

Stood 2 hours-----0.147

Stood 3 hours-----0.143

The filtrates were treated with BaCl_2 and allowed to stand 24 hours. Only a mere trace of precipitate appeared in either case. Therefore, precipitation is practically complete in 2 hours. Some experiments in the following table were made to compare results with the results from evolution methods. The steels used gave by the aqua regia method 0.125 and 0.114 per cent of sulphur.

Absorbent Used.	Per cent Sulphur	
	0.125	0.114
HCl(1.10) saturated with Br-----	0.104 0.114	0.106 0.105
Pure NaOH containing NaBrO_3 -----	0.108	0.114 0.106 0.108
Alkaline Pb. solution. PbS oxidized by HCl + KClO_3 and sol. ppted. by BaCl_2 -----		0.103
Ammoniacal CdCl_2 . The Cds dissolved in HCl + Bromine and ppted. by BaCl_2 -----		0.103 0.116

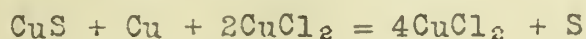
The results of the last four determinations agree fairly with those of the oxidation method and show that the concentrated solution of FeCl_3 has no appreciable solvent action on BaSO_4 in the presence of BaCl_2 . The chief disadvantage of the aqua regia method is the time required for the necessary solutions and evaporations. It takes nearly two days to complete the operation.

The Bamber⁽⁶⁾ method allows more field for manipulation and gives excellent results. A 2 gram sample of drillings is dissolved slowly in nitric acid in a platinum dish covered with a cover glass. When the sample is completely dissolved, the cover is removed and 1 gram of KNO_3 is added. Then evaporate to dryness and ignite at a good red heat for 3 or 4 minutes, turning the dish so that the sides as well as the bottom are red. 50 cc. of a 1 per cent solution of Na_2CO_3 are added, the contents boiled a few minutes, then filtered, using paper pulp and washed with a hot 1 per cent Na_2CO_3 solution. Acidify the filtrate with HCl and evaporate to dryness. Take up in 50 cc. of water and 2 cc. of HCl , filter, wash and precipitate the sulphur in the filtrate with barium chloride. This method was recommended by the committee on standard methods of iron analysis.⁽⁷⁾

Pulsifer⁽⁸⁾ proposed the following method: 2-1/2 grams of the sample are placed in a beaker and moistened with water. 20 cc. of chloric acid (1.12) and a few drops of hydrofluoric acid are added. After the action has subsided 5 cc. of HCl are added and the solution is boiled and filt-

ered. To the filtrate 20 cc. of HCl is added and the solution is evaporated with constant shaking to 10 cc. The residue on the filter is fused with Na_2O_2 in a nickel crucible, dissolved in 50 cc. of water, a little HCl added, filtered, and the filtrate added to the original one. The sulphuric acid is now precipitated with BaCl_2 . It is necessary to drive off all the HFl. The results are claimed to be very accurate.

Meineke⁽⁹⁾ proposed a method based on these reactions:



5 grams of iron are dissolved by 50 grams of copper ammonium chloride in 250 cc. of water containing 10 to 15 cc. HCl. The solution is kept nearly boiling until all the copper is redissolved, generally, about 15 minutes, and filtered at once through asbestos. The residue is treated with a little KClO_3 , 5cc. of HNO_3 (1.4), and 10 cc. of HCl (1.19), evaporated to dryness, redissolved, filtered and the sulphuric acid precipitated with BaCl_2 .

Boucher⁽¹⁰⁾ modifies Meineke's method by dissolving the residue in aqua regia or bromine, filtering, neutralizing the filtrate with NaOH, then making slightly acid with HCl, and adding BaCl_2 . He gives the following results by two methods:

	Aqua Regia Method Per cent of Sulphur	This Method Per cent Sulphur.
1. Bessemer iron-----	0.035 -----	0.041
2. " " -----	0.012 -----	0.021
3. " " -----	0.022 -----	0.024
4. " " -----	0.023 -----	0.023
5. " " -----		0.020 0.021
6. Mottled " -----	0.185 -----	0.191 0.192

Eggertz⁽¹¹⁾ gives the following method: 5 grams of iron are added to a solution of 10 grams of $KClO_3$ in 200 cc. of H_2O in a 50 cc. flask. Cover the flask with a small funnel and heat to boiling, then add 60 cc. of $HCl(1.12)$, evaporate to dryness, take up in HCl , filter and precipitate the sulphur in the usual manner.

Ericson⁽¹²⁾ gives a modification of the Garius method for sulphur in organic compounds, which is recommended for making standards and check work. Put 3 grams of borings into a hard Bohemian glass tube, like a combustion tube, sealed at one end. Add 25 or 30 cc. of strong HNO_3 and 5 cc. of HCl , draw the other end to a capillary and seal. Heat on a water bath 2 hours, then cool and break the capillary. Add 5 or 10 cc. of diluted HCl , boil 5 minutes, transfer to a casserol, neutralize with Na_2CO_3 and precipitate with $BaCl_2$.

Stehman⁽¹³⁾ gives an application of Eschka's method to pig irons. The oxidation in the wet way does not, with

some irons, effect the complete oxidation of the sulphur, a portion of it remaining with the residue of graphite and silica. Bamber's method is generally used when the oxidation method does not effect its purpose, and, no doubt, is the safest besides doing away with the precipitation of the sulphur from a concentrated solution of ferric chloride. The writer thought that if it were possible to reduce the pig iron to a fine powder, its oxidation might be effected in the presence of a basic mixture, the sulphur converted into the sulphates of the bases present, and the small amount of sulphides formed could be oxidized by bromine.

Two oxidizing mixtures were made as follows: One of magnesia, 2 parts and Na_2CO_3 , 1 part, well ground and mixed, and another of magnesia, 4 parts, K_2CO_3 , 1 part, and Na_2CO_3 1 part. The addition of K_2CO_3 , it was thought, would hasten the oxidation as it has a slight solvent action on ferric oxide. It was first thought that the samples had to be ground very fine and an agate mortar was used. After a little experimenting, it was found that samples of 80 and 60 mesh were oxidized completely, while samples of 30 mesh were not. In fact, 50 mesh seemed to be the limit of coarseness of the sample. For carrying out these experiments, four samples of grey iron were crushed in a steel mortar to a fineness of 80 and 60 mesh.

The following method was finally decided upon: 3 grams of the sample of a fineness higher than 50 mesh are weighed into a platinum crucible of 30 cc. capacity and 3

grams of the basic mixture added, mixing thoroughly and covering with about .5 gram. The crucible is placed over a Bunsen burner, using a shield of asbestos to protect the contents from the products of combustion of the flame and heated for one hour at a full red heat. At the end of this time the mass will be sintered together and can be broken up with a glass rod and extracted with hot water. 10 cc. of bromine water are added to the solution. It is then boiled for 10 minutes and filtered, taking care that the filtrate is clear. Add 1.5 cc. of HCl to the filtrate, boil to expel the bromine and precipitate the sulphur as usual. It was decided to treat samples Nos. 1 and 2 by each of the following methods.

First. Evolution method. Absorption of H_2S in a solution of KOH, oxidation of the K_2S formed by $KMnO_4$ solution, acidifying with HCl, clearing with oxalic acid, neutralizing with NH_4OH , making slightly acid with HCl and precipitating as usual. The sulphur in the residue was also determined and added to that obtained as H_2S . 10 grams of the sample were used.

Second. Oxidation in the wet way by solution in con. HNO_3 with the addition of 3 grams of $KClO_3$ after solution was complete, and the usual evaporation and resolution with the final precipitation of the sulphur in 100 cc. of solution with a hot saturated solution of $BaCl_2$. The precipitate was allowed to settle 12 hours.

Third. The Bamber method as described by Blair.

Sample No. 1

Evolution Method	HNO ₃ + KClO ₃	Bamber's Method	Basic Mixture	Time of Ignition	Fineness of Sample	Mixture Used
0.035	0.036	0.075	0.039	1.5 hr.	80 mesh	MgO + Na ₂ CO ₃
0.036	0.035	0.036	0.039	1.5 "	" "	" "
0.036	0.035	0.034	0.040	1 "	" "	" "
0.035	-----	0.035	0.042	1 "	" "	" "

Sample No. 2

0.032	0.032	0.030	0.031	1 hr.	60 mesh	MgO, Na ₂ CO ₃ + Na ₂ CO ₃
0.032	0.030	0.031	0.031	45 min.	" "	" " "
0.032	0.030	-----	0.032	1 hr.	" "	" " "

Sample No. 3

0.066	0.075	0.076	0.077	1 hr.	60 mesh	Not given
-----	0.075	-----	0.076	30 min.	" "	" " "
-----	0.076	-----	0.076	1 hr.	" "	" " "

Sample No. 4

0.043	0.058	0.054	0.054	1 hr.	80 mesh	Not given
-----	0.055	-----	0.057	1 "	60 "	" " "
-----	0.058	-----	0.056	1 "	" "	" " "

In samples Nos. 3 and 4, the sulphur has been determined by prominent chemists. There is no decided advant-

age in the use of a shield when gasoline gas is used and care is used to keep the flame from the mouth of the crucible. The use of K_2CO_3 shows no gain in action or time. It was thought that white iron would not lend itself as readily to oxidation but samples of white irons treated in the same way were oxidized as completely and in the same way as grey irons.

Sample of White Iron

Bamber's method ----	0.431	0.432	0.429
Oxidation with Basic Mixture-----	0.432	0.430	0.430

Phillips⁽¹⁴⁾ gives a series of experiments in fusing the finely divided iron with a mixture of an alkaline carbonate and nitrate. The fused mass is dissolved in water and the sulphur precipitated. He gives the following comparative results:

Character of Iron Used.	Fusion Mixture	Per cent of Sulphur by Fusion	Per cent of Sulphur by Oxidation with HNO_3
White iron crushed in a mortar and sifted through bolting sheeting	Equal parts of Na_2CO_3 + $NaNO_3$	0.112	0.101
		0.112	0.098
		0.114	0.100
		0.114	0.102
White iron crushed and sifted	45 parts $NaNO_3$ 45 " Na_2O_2 10 " Na_2CO_3	0.155	0.143
		0.150	0.149
		0.130	0.143
		0.139	0.147
Ferro manganese crushed and sifted	Equal parts of $NaNO_3$ and Na_2CO_3	0.022	0.012
		0.027	0.013
		0.018	0.012
		0.018	0.010
Grey iron powdered by rubber and plate	Equal parts of $NaNO_3$ and Na_2CO_3	0.034	0.027
		0.030	0.030

From these experiments there seems to be some reason to suppose that not quite all the sulphur of the iron is converted into BaSO_4 when the metal is oxidized by HNO_3 ; that it is completely recovered by the process of fusion can not be positively asserted.

Gravimetric Evolution Methods.

Karsten was the first to suggest dissolving iron or steel in HCl or H_2SO_4 , and collecting the evolved H_2S by absorbing it in a metallic salt solution. He recommended CuCl_2 .

Blair⁽³⁾ absorbs the H_2S in 20 or 30 cc. of a potassium hydrate solution of lead nitrate. He dissolves 10 grams of the sample in 1:1 solution of HCl as quickly as possible in a current of hydrogen. He collects the precipitate of PbS in a filter, washes it with hot water, then treats it with 5 to 20 cc. of HCl and some KClO_3 , allows it to stand until the fumes have partly passed off, adds about twice the volume of water and filters. He heats the filtrate to boiling and precipitates the sulphur from a slightly acid solution and allows it to stand a half hour before filtering. The whole operation takes about two and one-half hours.

Morrel⁽¹⁵⁾ passes the evolved H_2S into an ammoniacal solution of cadmium sulphate. The precipitate of CdS is filtered, washed with water containing a little ammonia, dried at 100 degrees C. and weighed. Five tests made on a piece of Bessemer steel known to contain .13 per cent S. gave (1) 0.124; (2) 0.125; (3) 0.137; (4) 0.125; (5) 0.124.

Berzelius⁽³⁾ proposed the use of a dilute solution of AgNO_3 made alkaline by ammonia as an absorbent. The precipitate of silver sulphide is washed, dried and redissolved in HNO_3 . The silver is then precipitated with HCl and filtered off. Add a little Na_2CO_3 to the filtrate and evaporate it nearly dry, dilute, add a few drops of HCl , filter if necessary, and add BaCl_2 to the filtrate.

Fresenius⁽⁵⁾ suggested passing the gas into a solution of bromine in HCl . Heat to drive off the bromine, neutralize with NH_4OH , and precipitate as usual. This process has the disadvantage of filling the room with fumes of bromine unless the apparatus is placed under a hood with a good draft.

Drown's method⁽¹⁶⁾ This is perhaps the best evolution method. The gases may be evolved very fast. A solution of KOH and KMnO_4 in equal proportions is used for the absorbent. The purple color of the KMnO_4 gradually changes to the green of the manganate. The solution is rendered colorless before precipitation with BaCl_2 either by evaporating to dryness and separating the silica, or by adding enough HCl to get a clear solution by the aid of heat, afterwards neutralizing the excess of acid with NH_4OH .

Craig⁽¹⁷⁾ suggested the use of an ammoniacal solution of H_2O_2 as an absorbent. After all the sample is dissolved, air is blown through the apparatus a few minutes, the solution is acidified with HCl and BaCl_2 added. The whole operation may be completed in two hours. For nearly two years the author added an excess of KClO_3 to the residue left and

precipitated the sulphur and only once obtained a trace.

Schulte(18) uses cadmium acetate as the absorbent. 32-35 cc. of a solution containing 25 grams of cadmium acetate and 250 cc. of acetic acid in a liter is used. 100 cc. of HCl 1.19 specific gravity, is used as the solvent. The acid is let in slowly and the mixture is heated gradually. After all the H_2S is evolved, 5 cc. of a copper sulphate solution containing 120 grams crystalized copper sulphate and 120 cc. of pure H_2SO_4 in a liter is added. The CuS is filtered off, washed and ignited to CuO and weighed. The weight of the CuO multiplied by 0.4030 gives the weight of the sulphur evolved.

Schindler(19) gives some experiments which show that if strong HCl(1.19 specific gravity) is used, the results by the evolution method are much higher than if an acid of only about half that strength (1.10 specific gravity) is used. In one method the gases were passed through a wash bottle containing a saturated solution of bromine in HCl and a second bottle containing bromine water. The contents of the two bottles were evaporated to dryness after the addition of 5 cc. of soda solution, taken up in water and filtered, the sulphur being precipitated in the filtrate. In the second method the gases were led through HBr in one and H_2O_2 in the second bottle.

Using HCl 1.19

Using HCl 1.10

Bromine Method	H_2O_2 Method	Bromine Method
A.O.070	0.071	0.048
A.O.071	0.067	0.048
B.O.221	-----	0.149
B.O.216	-----	0.149

When using the weaker acid, much sulphur was left in the residue, while, when using the stronger acid only a trace of sulphur was found in one case.

Phillips⁽¹⁾ proposed a method by which results obtained by the evolution method for white cast iron accorded well with those of the aqua regia method in Blair.

In white irons the sulphur exists in a form which is not readily changed to H_2S by the ordinary evolution method. Thus, low results are obtained by the ordinary method. The iron was dissolved by HCl 1.12 with a slow stream of CO_2 passing through the apparatus, heat being applied as the action became slower. The mixed gases were passed through a porcelain tube heated to dull redness, whereby the gases of the $(CH_3)_2S$ type and the hydrosulphides were converted into H_2S . The gases then pass through a nitrogen flask containing a solution of bromine in HCl and then to the bottom of an 8-liter flask containing a little of the same solution. This large bottle is necessary for the complete condensation of the sulphuric acid. The sulphur was precipitated from the solutions as $BaSO_4$. The evolution flask must be heated at least 2 hours. In the following table means of several experiments are given, using the old evolution method, this one, and the aqua regia method.

Old Evolution Method % S	This Evolution Method % S	Aqua Regia Method % S
A. 0.052	0.099	0.100
B. 0.094	0.180	0.171

Volumetric Evolution Methods

Blair, in his Chemical Analysis of Iron, gives the following method. Dissolve 5-10 grams of the steel in 100cc. of 1 to 1 acid in an atmosphere of hydrogen. Pass the evolved gases into 50 cc. of KOH(1.1 specific gravity); when the evolution is complete, dilute the KOH with water to 500 cc. then acidify with HCl and titrate at once with a standard solution of iodine, the sulphur equivalent per cc. of which is known.

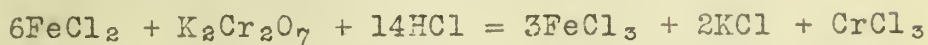
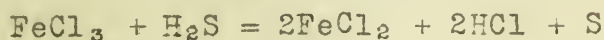
There are several disadvantages to this process. G. Naske⁽²³⁾ made the following remarks on the process. "When the gases are passed into caustic soda solutions, according to the degree of concentration, a varying mixture of Na_2S and NaHS , as well as various polysulphides are formed. The solutions of Na_2S are easily decomposed and even contact with the air converts it into thiosulphate. At a higher temperature a portion of the sulphur is oxidized to sulphuric acid and as steam passes over into the receiver; the temperature is always high. H_2S also escapes into the air. Therefore, results are low when NaOH is used as the absorbent."

Hopper⁽²⁰⁾ gives the following method which he claims is very rapid and gives good results. The H_2S is absorbed in NaOH and the quantity of S is determined by adding a standard solution of lead nitrate until no precipitate of PbS is formed.

Compredon⁽²¹⁾ passes the evolved gases through a red hot tube together with hydrogen and carbon dioxide, then

collects the gases in a slightly acid solution of zinc acetate. He titrates the ZnS with a standard iodine solution. The process may be accomplished in a half hour.

Boucher⁽²²⁾ method. The H_2S absorbed in NaOH is run into an acid solution of FeCl_3 ; H_2S is liberated and a portion of the iron is reduced. The reduced iron is determined by standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution.



By dissolving 3.065 grams of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 liter of water, a solution is obtained, 1 cc. of which equals .001 gram of Sulphur. The following table shows the results of several tests.

Sample Number	Gravimetric Method. Per cent Sulphur	$\text{K}_2\text{Cr}_2\text{O}_7$ Method Per cent Sulphur.
1	0.041	0.038
2	0.015	0.017
3	0.020	0.023
4	0.028	0.030

The process takes from one-half to three-quarters of an hour.

Treadwell,⁽²³⁾ Crobaugh,⁽²⁴⁾ and Riemer,⁽²⁵⁾ absorb the H_2S in CdCl_2 solution, acidify and titrate with iodine solution. Riemer considers this the best volumetric method.

When titrating⁽²⁶⁾ the absorbed H_2S with iodine solution, CdCl_2 solution used as the absorbent gives better results than NaOH solution.

NaOH Solution Per cent Sulphur	CdCl ₂ Solution Per cent Sulphur
0.038	0.047
0.039	0.047
0.042	0.049

Herting(27) obtained satisfactory results with the method of Blair, of absorbing the H_2S in a cadmium salt solution, collecting the CdS on a filter, adding it to a $N/20$ iodine solution and titrating the excess of iodine with thiosulphate solution. Time required for the process, one hour.

McFarlane⁽²⁸⁾ and Gregory Method. It is a well known fact that only a part of the sulphur in pig iron is evolved as hydrogen sulphide when treated with acid. Annealing the powdered sample before treating it with acid gives higher results. 5 grams of the powdered sample were treated with about a half gram of cream of tartar, the mixture wrapped in a filter paper and placed in a small crucible. The crucible is covered and heated to a bright red heat in a muffle for fifteen minutes, cooled, broken up and placed in the evolution flask. The evolved gases were absorbed in $CdCl_2$, acidified and titrated directly with iodine. The following results were obtained by the aqua regia and evolution methods.

Pig Iron

	Aqua Regia Method Per cent Sulphur		Evolution Method Per cent Sulphur	
1	0.090	0.090	0.091	0.094
2	0.096	0.098	0.093	0.095
3	0.066	0.066	0.066	0.068

Chilled Shot

1	0.186	0.188
2	0.197	0.204
3	0.115	0.113

Colorimetric Methods

Colorimetric methods are used in laboratories where it is necessary to make many analyses. They give only approximate results.

Arnold and Hardy⁽²⁹⁾ evolve the sulphur as H_2S and absorb it in $NaOH$, then add 10 cc of lead acetate solution to the $NaOH$. A brown color due to PbS is produced and the depth of the color is proportional to the amount of sulphur present. After shaking, the mixture is placed in a Nessler tube and compared with standards made from lead acetate and H_2S water. From the results of numerous experiments, where sulphur had been determined as $BaSO_4$, the possible errors in steels ranging from .01 to .04 per cent of sulphur, were shown never to be over .01 per cent; in steels containing .06 to .10 per cent, as far as .02 per cent; and those containing from .11 to .14 per cent, occasionally as much as .03 per cent. This process is not applicable where accurate

work is necessary.

(30)
Treadwell Method. The H_2S is passed through a cloth saturated with cadmium acetate solution. A yellow color owing to the formation of CdS is produced; the intensity of the color being proportional to the amount of H_2S . The color of the cloth is compared with standards.

SUMMARY

1. The aqua regia method, when properly manipulated, gives the most reliable results.

2. All the sulphur is not evolved as H_2S when the iron is dissolved in acid, and low results are obtained by the ordinary evolution methods.

3. Of the rapid methods, that one where the H_2S is absorbed in $CdCl_2$ gives better results than when absorbed in $NaOH$ or KOH .

4. When an evolution method is used, higher results are obtained if the sample is annealed before being dissolved.

5. Higher results are obtained by fusing the finely divided sample with a strong base, than by use of the aqua regia method.

6. If the sulphur is precipitated from a boiling solution, the solution should be strongly acid. Better results are obtained by precipitation from a nearly neutral cold solution and allowing it to stand 24 hours.

OBJECT.

All the accurate methods so far described have the disadvantage of a long manipulation. About two days are required for the standard method. Numerous rapid methods have been proposed, but they all give low results. The purpose of this investigation was to try to devise a method which would be accurate and, at the same time, rapid.

So far as found in the available literature, Blount⁽³²⁾ has done the only work on heating the steel directly

and trying to evolve the sulphur as sulphur trioxide and sulphur dioxide. He heated the drillings to nearly 1,200 degrees C. in a porcelain tube in a current of oxygen. The products of combustion were led into baryta water. The baryta water containing the barium carbonate, sulphate and sulphite in suspension, was acidified with HCl, saturated with bromine and the BaSO_4 determined as usual. It was an easy matter to collect and estimate all the sulphur evolved, but it was not possible to expel all the sulphur from the magnetic iron oxide. It was found that a core of unoxidized steel was left in the center, into which the sulphur seemed to be driven. It was thought that this method could be improved upon by using a platinum crucible in the place of a porcelain tube as a much higher temperature could be attained.

EXPERIMENTAL

An analysis of a steel sample for sulphur, phosphorus, silicon, manganese, and carbon was made. The following methods were used:

Sulphur: Evolution method of Blair.-5 grams of the steel was dissolved in 100 cc. of dilute HCl, the evolved gases were caught in KOH, the solution diluted to 500 cc., acidified and titrated with iodine solution.

Sulphur: Aqua regia method of Blair with modifications as given before.

Phosphorus: 2 grams of the sample was dissolved in 50 cc. of HNO_3 (1.13 specific gravity), 10 cc. of con. HCl were added and the solution evaporated to dryness. The residue was then baked until free from HNO_3 , taken up in 30 cc. of HCl, diluted to about 60 cc. and filtered. The filtrate was evaporated to about 25 cc., 20 cc. of con. HNO_3 added, and again evaporated until film began to form. 30 cc. of dil. HNO_3 were then added and the solution diluted to 150 cc. When between 70 and 80 degrees C., 50 cc. of molybdate solution was added. The yellow precipitate was collected in a filter, washed and then dissolved in 30 cc. of NH_4OH , 1 part of NH_4OH to 4 parts of water. The solution was acidified with 30 cc. of H_2SO_4 , one volume of H_2SO_4 to 2 volumes of water, and then run through a Jone's reductor. The solution was then titrated immediately with KMnO_4 .

Manganese: Method of Noyes and Clay. 1.5

grams of the steel was dissolved in 25 cc. of dilute HNO_3 and 5 cc. of con. HCl . The solution was made nearly neutral with Na_2CO_3 and an excess of an emulsion of ZnO added to precipitate the iron. The mixture was made up to 300 cc. and filtered. 200 cc. of the filtrate was taken, 20 cc. of sodium acetate and 40 cc. of bromine water added and heated until MnO_2 formed. The MnO_2 was filtered off and dissolved in standard ferrous ammonium sulphate. The solution was titrated with KMnO_4 .

Silica: The residues from the gravimetric sulphur determination were taken and purified as usual.

Carbon: 3 grams of the sample were dissolved in 200 cc. of potassium copper chloride and 15 cc. of HCl . The residue was filtered on asbestos and ignited in a combustion tube. The CO_2 was absorbed in soda lime and weighed. The following table shows the results obtained on Bessemer .40 of the Bureau of Standards. The first row of analyses are those obtained in the Bureau and the rest are those obtained by the above methods.

	Per cent S. Evolution Method	Per cent S. Aqua Regia Method	Per cent C.	Per cent Mn.	Per cent Si.	Per cent P.
Standard	0.110	0.118	0.427	0.872	0.045	0.116
Found	0.062	0.103	0.462	0.606	0.040	0.108
	0.069	0.110	0.447	0.611	0.046	0.117
	0.061	0.117				0.108
	0.073					
	0.058					
	0.058					
	0.072					
	0.069					

The purpose was to determine carbon and sulphur at the same time by ignition of the sample in a current of oxygen. The following train was used after the combustion chamber: (1) A tube of platinized asbestos to oxidize the sulphur dioxide to the trioxide; (2) A U-tube partially filled with an almost saturated solution of chromic acid to absorb the sulphur trioxide; (3) A U-tube of CaCl_2 to absorb the moisture; (4) A U-tube of anhydrous copper sulphate to take up chlorine, if present; (5) A U-tube of fresh soda lime to absorb the CO_2 ; (6) A U-tube with soda lime in the right arm and CaCl_2 in the left. A platinum tube about 16 inches long and 1 inch in diameter was used at first. The sample was placed in a porcelain boat on a layer of Al_2O_3 . The boat was placed in the middle of the tube and heated with the full flame of a blast. The ends of the tube were kept cool by means of a lead coil, through which water circulated, so as not to burn the rubber stoppers. The stoppers were protected from radiation from the inside by perforated porcelain discs ground to fit the tube rather snugly. Several combustions were made with this tube, but no satisfactory carbon determinations were obtained as the following table shows.

No. of Sample	Per cent of Carbon
B. .40	0.341
"	0.447
"	0.332
.60	0.340
"	0.433
"	0.417

A modified Gooch tabulated platinum crucible was then used and found to give excellent results for carbon. The sample was placed in a little bucket made of platinum foil. A layer of Al_2O_3 was used to protect the platinum. The bucket was placed in the crucible and the lid sealed air tight with sodium tungstate.

The chromic acid used was made free from sulphur by first washing with con. HNO_3 and then allowing the aqueous solution to stand over BaCrO_4 several hours. The Al_2O_3 was also purified in the laboratory.

The sulphur absorbed in the chromic acid was determined by diluting the solution to about 100 cc., adding 2 cc. of HCl and precipitating as usual. The method was unsatisfactory, as the BaSO_4 was contaminated when precipitated. The following test was made on the method. A solution of K_2SO_4 was made and its content of sulphur per cc. determined. A known amount of this solution was added to the same amount of chromic as used in the U-tube, the mixture diluted and the sulphur precipitated as usual. The following results were obtained.

Grams of S. Taken	Grams of S. Found
0.00056	0.00071
0.00056	0.00060
0.00056	0.00118
0.00056	0.00192
0.00056	0.00175
0.00056	0.00204

The chromic acid in the U-tube was then replaced by a saturated solution of BaCrO_4 in 2 per cent HCl . If, to an HCl solution of barium chromate, a solution containing sulphates is added, the sulphuric acid radicle combines with the barium and sets free an equivalent amount of chromic acid.⁽³⁰⁾ Barium chromate is entirely precipitated by NH_4OH . If, then, the solution is neutralized, the barium chromate is precipitated and a quantity of ammonium chromate, equivalent to the sulphate introduced, remains in solution.

The following method was used to determine the free chromic acid: After the combustion, the contents of the U-tube were transferred to a beaker, diluted and made alkaline with NH_4OH . The precipitate of BaCrO_4 was filtered off and washed. The filtrate was made acid with H_2SO_4 , a known amount of ferrous ammonium sulphate solution added, and the excess titrated with KMnO_4 solution. The iron equivalents of both solutions being known, their difference represented the iron equivalent of the free chromic acid. This was calculated over to sulphur by a simple proportion.

The BaCrO_4 used was made by adding BaCl_2 to the aqueous solution of sulphur free chromic acid. The following tests were made on the method, the sulphur being introduced in the form of K_2SO_4 .

Wt. of S. Taken

Wt. of S. Found

0.0028

0.0017

"

0.0019

"

0.0021

"

0.0022

"

0.0023

"

0.0018

"

0.0022

"

0.0023

The method seemed to be satisfactory. Our great trouble was to find a suitable compound to protect the platinum from the iron and not combine with the sulphur. Al_2O_3 is all right for carbon determinations, but it seems to combine with a part of the sulphur and not permit it to be volatilized.

The following table shows the percentage of sulphur volatilized when using Al_2O_3 from a steel containing .080 per cent sulphur, after igniting 30 minutes.

No. of Sample	Per cent Sulphur
1	0.009
2	0.008
3	0.007

SiO_2 free from sulphur was next tried. This gave much higher results but the sample was only ignited 15 minutes for fear that the slag formed would attack the platinum.

No. of Sample	Per cent Sulphur	Per cent in Iron residue
1	0.015	-----
2	0.017	-----
3	0.037	-----
4	0.027	0.065
5	0.013	0.082

In samples 4 and 5, the sulphur was determined in the silica, but only a trace was found.

As it is claimed that all the sulphur remains in

the residue after dissolving the steel in potassium copper chloride, the method of burning this residue in a combustion tube and collecting the SO_3 evolved in the same manner was tried.

	No. of Sample	Per cent Sulphur Gravimet- rically	Per cent Sulphur Combust- ion
Bessemer	.60	0.075	0.066
"	"	0.075	0.015
"	"	0.075	0.020
"	"	0.075	0.028
"	"	0.075	0.017
Open Hearth	.20	0.020	0.004
"	"	0.020	0.007

Two residues left after 3 grams of steel were dissolved in copper potassium chloride and 10 cc. of HCl were burned in the combustion crucible and the sulphur evolved determined.

	Per cent S. present	Per cent S. found
No. 1	0.075	0.036
No. 2	0.075	0.027

These results show that the sulphur was not all evolved or some was lost as H_2S by the action of the HCl used to help dissolve the steel.

Some clay crucibles were moulded and burned to try in the place of the platinum bucket, as a receptacle for

the steel. A basic fire clay was first tried, the steel being put in it and a layer of SiO_2 outside between it and the platinum crucible. After heating a half hour, the iron had gone through the clay, slagged with the SiO_2 and attacked the crucible. Some crucibles were then prepared from an acid clay, which seemed to work satisfactorily. When heated for an hour in a porcelain crucible with a layer of SiO_2 , the iron did not slag with the SiO_2 .

Two samples of steel ignited with the full blast as above for 30 minutes and one hour respectively, were tested for sulphur. A considerable portion of sulphur was found in each case.

CONCLUSION

The following conclusions may be drawn from these investigations:

1. The sulphur is not evolved quantitatively when the steel is heated directly with a blast lamp for an hour.
2. The absorption of the SO_3 in an HCl solution of BaCrO_4 , and the titration of the chromic acid set free, offers a rapid and accurate method for the determination of the sulphur evolved.
3. More sulphur comes over when an acid substance is used to protect the crucible, than when a basic substance is used.

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R. M. Stiff.

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